PCT/NL 2004 / 000499

Europäisches Patentamt | European Patent Office | Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03077183.6

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Anmeldung Nr:
Application no.: 03077183.6
Demande no:

Anmeldetag:
Date of filing: 10.07.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Wageningen Universiteit
Bomenweg 2
6703 HD Wageningen
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Process for producing hydrogen

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C12P3/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

Process for producing hydrogen

The present invention relates to a process for the biocatalysed production of hydrogen from bio-oxidisable material.

Introduction

The effects of global warming and the depletion of the fossil fuels has led to an enormous amount of research in the field of new energy carriers. These new energy carriers have to be renewable and preferably suitable as a transportation fuel. Many regard hydrogen gas as a candidate for the future energy economy: the Hydrogen Economy. Hydrogen gas can be used in fuel cells, which can convert the hydrogen to electricity in a high yield (approx. 60%).

Conventional (chemical) methods for the production of hydrogen gas still rely on the conversion of non-renewable materials (e.g. natural gas). Examples of such methods are steam reforming (0.40 Nm^3 methane per Nm^3 H_2), methanol cracking (0.59 Nm^3 methane per Nm^3 H_2) and water electrolysis (1.3 Nm^3 methane per Nm^3 H_2) [Stoll RE, von Linde F, Hydrocarbon Processing, December 2000:42-46].

A lot of research has been dedicated to the biological production of hydrogen gas from renewable sources, such as energy crops. Polysaccharides and ligno-celluloses from those energy crops can be hydrolysed to form hexoses and pentoses, which can be converted to hydrogen gas by fermentation subsequently. Glucose, for example, can be theoretically converted according to:

$$\text{Glucose} + 6\ H_2O \rightarrow 12\ H_2 + 6\ CO_2 \qquad \text{Reaction 1.}$$

Only under favourable temperatures and hydrogen concentrations will this reaction yield enough energy for cell growth. It has been calculated that at a temperature of 60 °C a hydrogen pressure as low as 50 Pa is needed for reaction 1 to be favourable for cell growth [Lee MJ, Zinder SH, Applied and Environmental Microbiology, 1988;54:1457-1461]. Currently, there is no economically feasible method available of achieving such low hydrogen pressures. The conditions required are less extreme when part of the glucose is converted to fatty acids (e.g. acetic acid):

$$\text{Glucose} + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO \qquad \text{Reaction 2.}$$

But even then the hydrogen pressure has to be as low as 2,000-20,000 Pa (at 70 °C) in order to be favourable for cell growth [Groenestijn JW et al., International Journal of Hydrogen Energy, 2002;27:1141-1147] and only one third of the influent bio-oxidisable material (COD: Chemical Oxygen Demand) is converted to hydrogen gas. The remaining two third of the COD is available as acetic acid and still needs to be converted to hydrogen gas to achieve 100% conversion. For this purpose a two stage process known as "the hydrogen factory" was developed. This biological process

consists of a dark stage and a light stage. In the dark stage (hyper)thermophilic microorganisms convert sugars to hydrogen gas and fatty acids according to reaction 2. As explained, it is critical to keep the hydrogen pressure below 2000-20000 Pa (at 70 °C) for the reaction to proceed. There are several methods to achieve this low hydrogen pressure, but all methods are energetically and/or economically costly.
Subsequently, the fatty acids are converted to hydrogen gas in the light stage by mesophilic photoheterotrophic bacteria. A problem with this light stage, that still has not been overcome, is that the process is severely limited by the amount of (sun)light that can be introduced into the reactor to get economically feasible conversion rates. A further overall problem is that a hydrogen/CO_2 gas mixture is produced which has to be separated.
Bioelectricity has been another approach to the development of a society based on sustainable energy. Some known microorganisms are able to use electrodes as electron acceptor. So, instead of using for example oxygen as a direct electron acceptor, the microorganisms donate their electrons directly to an electrode.
This principle allows for a biofuel cell process set-up: bio-oxidisable material (COD) is converted in the anodic compartment, while anodophilic bacteria transfer electrons to the anode. E.g. for glucose:

$$\text{Glucose} + 6\ H_2O \rightarrow 6\ CO_2 + 24\ H^+ + 24\ e^- \text{ (Biocatalysed)} \qquad \text{Reaction 3a.}$$

In the cathodic compartment electrons are transferred to oxygen from the cathode:

$$6\ O_2 + 24\ H^+ + 24\ e^- \rightarrow 12\ H_2O \qquad \text{Reaction 3b.}$$

The anode and the cathode are connected by an electrical circuit and the anodic and cathodic compartments are separated by a proton permeable membrane. Kim et al. showed that it was possible to generate electricity in such a biofuel cell using the metal reducing bacterium *Shewanella putrefaciens* growing on lactate [Kim et al., Enzyme and Microbial Technology, 2002;30:145-152; see also WO 01/04061].
In an open circuit set-up a potential built up to 0.6 Volt was measured. Furthermore, cyclic voltammetry tests with bacterial suspensions showed that the potential in the fuel cell could even be as high as 0.8 Volt. However, when the electrical circuit was closed and a resistance of 1000Ω was put in, Kim et al. detected an electrical current of approx. 0.02-0.04 mA, implying a potential of only 0.02-0.04 Volt.
Theoretically, a voltage of approximately 1.15 Volt can be achieved in a fuel cell working on lactate (1.23 Volt on glucose) under the conditions described by Kim et al., but because the microorganisms take a part of this energy for maintenance and/or cell growth, this maximum will never be achieved in a biofuel cell. However, the yield that Kim et al. achieved in their process set-up (0.04 Volt/1.15 Volt = 3.5%) is much lower than theoretically possible in this biofuel cell (0.8 Volt/1.18 Volt = 70 %), because in

their process set-up, by providing oxygen as the electron acceptor, the anodophilic microorganisms are given the choice to release the electrons at any energy level between 0 and 1.14 Volts. The lower the energy level the electrons are released, the more energy the microorganisms gain for themselves for use in maintenance and cell growth. So, by using oxygen as the electron acceptor in a biofuel cell, a selection criterion is being created that selects for microorganisms that release the electrons at low energy levels. The microorganisms that do so, outcompete the microorganisms that release the electrons at a higher energy level, because they keep more of the energy for themselves and can thus grow faster. The more energy from the bio-oxidisable material the anodophilic microorganisms take for themselves, the more energy is lost for electricity production and thus low yields are achieved in the biofuel cell as described by Kim et al.

Description of the invention

It was found that hydrogen can be produced in a bio-electrochemical process, by applying a potential between the anode and cathode of a bio-electrochemical cell that is necessary and sufficient for the electrons generated in the biochemical degradation of bio-oxidisable material to be transferred to protons and thus to generate molecular hydrogen.

Thus, the invention allows the ability of anodophilic bacteria to transfer electrons to an electrode to be used in a very effective and efficient process for the production of hydrogen gas from bio-oxidisable materials. In contrast to a biofuel cell, not oxygen, but hydrogen ions are used as the electron acceptor. At the anodic electrode bio-oxidisable material is converted as in the biofuel cell. As an example, the following reaction applies to glucose:

$$\text{Glucose} + 6\,H_2O \rightarrow 6\,CO_2 + 24\,H^+ + 24\,e^- \text{ (Biocatalysed)} \qquad \text{Reaction 3a.}$$

At the cathodic electrode electrons are transferred to hydrogen ions instead of oxygen, so that hydrogen gas is produced:

$$24\,H^+ + 24\,e^- \rightarrow 12\,H_2\,(g) \qquad \text{Reaction 3c.}$$

As another examples, he following reactions apply to hydrogen sulphide:

$$H_2S \rightarrow 2\,H^+ + S^0 + 2\,e^- \text{ (Biocatalysed)} \qquad \text{Reaction 4a.}$$

$$2\,H^+ + 2\,e^- \rightarrow 2\,H_2\,(g) \qquad \text{Reaction 4c.}$$

Under standard conditions, the Gibbs energy of this reaction for glucose is only slightly positive (approx. 3 kJ/mol glucose), meaning that energy is needed for this reaction to run and a voltage has to be applied (instead of produced by the microorganisms in a biofuel cell). In theory this would cost only approximately 0.01 Volt. However, because the microorganisms that catalyse this reaction also need energy for cell growth and

maintenance, the voltage has to be higher. By applying the right voltage between 0 and 1.23 V, just enough energy is provided to the anodophilic microorganisms to perform their maintenance and cell growth processes, while the remainder of the energy of the bio-oxidisable material is recovered as hydrogen gas. In this way a selection criterion is created that selects for microorganisms that release the electrons at a high energy level, meaning that high yields can be achieved of hydrogen gas production from bio-oxidisable material.

It was found that applying a (single-cell) potential between 0.05 and 1.5 volt, preferably between 0.1 and 1.2 V, more preferably up to 0.7 V and especially between 0.2 and 0.5 volt, allows an efficient production of hydrogen gas, while maintaining a sufficient growth and maintenance of the bacterial population. For an effective electron acceptance by protons, the pH in the bio-electrochemical reactor should be neutral to moderately acidic, i.e. between 3 and 9, preferably between 5 and 7.

Thus, by applying the right conditions in this biocatalysed electrolysis process for the production of hydrogen gas, a selection criterion is created for the right microorganisms to grow. This makes sterilisation of the influent unnecessary. The effective mixed culture of anodophilic microorganisms able to oxidise every bio-oxidisable material will arise, when the right voltage is applied. This effective culture can be obtained by starting with activated sludge populations or anaerobic populations, of which a suitable variety is abundantly present in conventional purification pants and biogas production plants, respectively. These populations are cultured under the conditions of the present process for a sufficient time for adaptation. Mesophilic populations, which are active at temperatures between e.g. 15 and 40°C are preferred, but thermophilic bacteria can also be used, if desired.

Because the invention selects for microorganisms that release the electrons at a high energy level, the anode will be covered with microorganisms of such kind. When this anode/anodic compartment is temporarily connected to a cathodic compartment provided with oxygen as described by Kim et al., a high yield biofuel cell is created, capable of converting bio-oxidisable material to electricity in a high yield. So besides being an efficient process for producing hydrogen gas from bio-oxidisable material, this invention also provides a way of selecting for anodophilic microorganisms, that release the electrons at a high energy level, and that can be temporarily used in a biofuel cell set-up as well. Because the selection criterion, as described earlier, is lost when switching to a biofuel cell mode, the anode will transform into a low yield anode in time. By switching back to the hydrogen production mode the high yield microorganisms are selected for again.

By switching between hydrogen production and biofuel cell mode efficiently, without losing too much of the high yield microorganisms in the biofuel cell mode, the

invention also provides a very efficient way to produce electricity from bio-oxidisable materials. By converting the produced hydrogen to electricity using a normal hydrogen fuel cell, a process that only produces electricity in high yields, is achieved. Accordingly, the electricity needed for the hydrogen production, to apply the voltage, can be obtained during the biofuel cell mode or by the conversion of part of the produced hydrogen to electricity in a normal fuel cell (approx. 60% yield). Overall COD yields as high as 60-85% can be obtained of COD conversion to hydrogen gas, which can compare to COD yields of conventional non-sustainable methods. While those methods are based on the conversion of valuable raw materials (e.g. natural gas (see above)), this invention can use every bio-oxidisable COD-containing (waste)stream as influent and convert it to hydrogen gas efficiently (see table 1.). As used herein, COD yield refers to the electron yield, i.e. the percentage of electrons in the hydrogen produced vs. the electron input.

Table 1. COD yields of conventional (chemical) hydrogen production methods compared to hydrogen production by biocatalysed electrolysis of bio-oxidisable COD-containing (waste) streams.

Hydrogen Production Method	COD Yield (%)	Raw Material
Biocatalysed Electrolysis	60-85	Bio-oxidisable COD-containing (waste)streams
Steam Reforming	63	Methane (Natural Gas)
Methanol Cracking	45	Methane (Natural Gas)
Water Electrolysis	19	Methane (Natural Gas)

The present invention can function without a membrane between the anodic and cathodic compartments in the hydrogen production mode, because a voltage is applied instead of generated by the microorganisms. Another advantage is that hydrogen (cathode) and carbon dioxide (anode) are produced separately from each other, in contrast with (hyper)thermophilic and mesophilic photoheterotrophic fermentation during which a hydrogen/ carbon dioxide mixture is produced. Accordingly, no extra energy has to be put into the separation of the gases. Also, a one stage process is achieved, instead of two stage as with "the hydrogen factory". Further, this process set-up gets around the light problem in the light stage of "the hydrogen factory", because no light is needed.

The present process can be carried out in a reactor having the characteristics of an electrolysis cell. The reactor comprises an anodic compartment and a cathodic compartment, separated by a semi-permeable membrane, a controllable power source to be connected to the anode and cathode, an inlet for bio-oxidisable material, a liquid effluent outlet, and an outlet for hydrogen gas, optionally with a hydrogen storage

facility. In the bimodal variant, wherein hydrogen production is alternated with hydrogen consumption (power generation), suitable inlets for hydrogen and oxygen are also provided.

The membrane is a non-conducting proton exchange membrane of a suitable, e.g. polymeric material as conventionally used in fuel cells. In case of hydrogen production only, the membrane may be dispensed with. The electrodes are dimensioned such that the cell can process 10 kg of COD per m^3 of reactor volume per day. The electrodes can be made of a metal or carbon or of a conductive polymer, e.g. containing copper or another metal or carbon. The anode compartment contains the anodophilic populations, which will grow on the anode surface. Thus, for example, the reactor can be set-up as a fixed film reactor in which the anode is used as a carrier.

In the bimodal mode, the hydrogen production and power production modes can be activated by simple operation of the relevant valves and connectors, as described below. It is preferred that the power supply mode is not operated continuously for more than 3 days, especially more than 24 hours, so as to avoid deterioration of the anodophilic population. Preferably the ratio of activation periods of the hydrogen production mode and the power generation mode is between 1:4 and 4:1, more preferably between 2:3 and 3:2. A very suitable regimen is a 24 hour cycle comprising 1 or 2 hydrogen production stages of 4-12 hours interrupted by power supply stages of 4-12 hours, for example. Hydrogen production (= power consumption) can advantageously take place at times of low general power consumption, especially at night, while the reverse applies to power generation.

A schematic diagram of a reactor according to the present invention is depicted in the accompanying Figure. The reactor comprises a rector cell 1, having an anode compartment 2 with anode 3, and a cathode compartment 4, with cathode 5, and a liquid inlet 6 for bio-oxidisable material. The cathode compartment has a liquid outlet 7 with a valve 8, a gas inlet 9 for oxygen (air) with a valve 10, and a gas outlet 11. The anode and cathode compartments are separated by a semipermeable membrane 12. The anode compartment has an outlet 13, which splits into a loop 14 towards the cathode compartment and a liquid outlet 15, with a valve 16. The loop 14 has a valve 17. The anode and cathode are connected to a power supply 19 or a power acceptor 20 with a selector 18 between 19 and 20 (at the anode side according to the figure). It should be stressed that the figure is only schematic and is not indicative of dimensions, nor restrictive as top further parts or variations.

In the hydrogen production mode A, valves 8 and 17 are open and valves 10 and 16 are closed, so that the flow of bio-oxidisable material can bypass the membrane 12 and the resulting effluent exits though 7, and no gas is added to the cathode compartment; selector 18 is connected to the power supply 19. Hydrogen gas is collected from outlet

11, and can be stored in stage facility (not shown), or directly be used in a hydrogen consuming process.

In the power generation mode B, valves 8 and 17 are closed and valves 10 and 16 are open, so that the flow resulting from conversion of the bio-oxidisable material is diverted to exit 15 and only protons can enter the cathode compartment through membrane 12, while air (oxygen) is fed to the cathode; selector 18 is connected to the power acceptor 20. Waste air escapes through outlet 11.

The reactor can be operated at autogenous temperature, i.e. without external temperature control, preferably between 15 and 40°C, more preferably between 25 and 39°C. The bio-oxidisable material can be any organic or inorganic material containing low-molecular-weight degradable or oxidisable compounds that can generally be treated in aerobic or anaerobic reactors; examples include saccharides, fatty acids, proteins, alcohols, carbon monoxide, hydrogen sulphide, elemental sulphur, etc. When using inorganic material, such as hydrogen sulphide, the bacteria are preferably autotrophic, while bacteria using carbonaceous material will be heterotrophic.

The appropriate population of anodophilic can be maintained by making use of the competition under the specific electron potential applied. Thus, by slight variation of the potential, the proper anodophiles having the desired electron-accepting properties can outcompete the less efficient anodophiles. Another parameter of adjusting the conditions in the reactor is the redox potential control; the redox potential should not be lower than about –350 mV (Ag/AgCl) so as to avoid unwanted methanogenesis.

The process described above for the production of hydrogen gas is also applicable with other than anodophilic organisms, such as *E. coli* by using electron mediators. An electron mediator is able to transport electrons from microorganisms to an electrode surface by switching between its oxidised and reduced form. Examples of such electron mediators are known to the skilled person and comprise aromatic redox compounds, or dyes, such as benzyl viologen, methylene blue, neutral red and the like. Such electron mediators can be used at concentrations of 5 – 500 μmol per l. So instead of direct transfer from the microorganism to the electrode, an indirect transfer takes place via the electron mediator.

Claims

1. A process for producing hydrogen from bio-oxidisable material by:
   - introducing the bio-oxidisable material into a reactor provided with an anode and a cathode and containing anodophilic bacteria in an aqueous medium;
   - applying a potential between the anode and cathode of between 0.1 and 1.5 volt, while maintaining a pH of between 3 and 9 in the aqueous medium;
   - collecting hydrogen gas from the cathode.

2. A process according to claim 1, in which the potential between the anode and cathode is between 0.2 and 0.7 volt.

3. A process according to claim 1 or 2, in which a pH of between 5 and 7 is maintained in the aqueous medium.

4. A process according to any one of the preceding claims, in which the anodophilic bacteria are derived from activated sludge and/or anaerobic sludge.

5. A process according to any one of the preceding claims, in which the anodophilic bacteria are replaced by or supplemented with non-anodophilic bacteria, and an electron mediator is present in the reactor.

6. A process according to any one of the preceding claims, in which, in a stage subsequent to the hydrogen production stage, electric power is produced by interrupting the application of the potential and passing oxygen to the cathode.

7. A process according to claim 6, in which the duration of the hydrogen production stages and the power production stages have a ratio of between 1:4 and 4:1.

8. A reactor suitable for carrying out the process according to any one of claims 1-7, comprising a reactor cell containing a anode compartment and a cathode compartment optionally separated by a proton-permeable membrane with a liquid loop for bypassing the membrane, a liquid inlet and one or more liquid outlets, a gas inlet and a gas outlet, and a power supply and optionally a power acceptor.

Abstract

A process for producing hydrogen from bio-oxidisable material is disclosed herein. The process comprises the steps of:

- introducing the bio-oxidisable material into a reactor provided with an anode and a cathode and containing anodophilic bacteria in an aqueous medium;
- applying a potential between the anode and cathode 0.05 and 1.5 volt, while maintaining a pH of between 3 and 9 in the aqueous medium;
- collecting hydrogen gas at the cathode.

The hydrogen production process can be intermittently switched to a hydrogen-consuming electric power generation stage (biofuel cell) by adding oxygen to the cathode and separating the anode and cathode spaces by means of a proton exchange membrane.

P209404EP

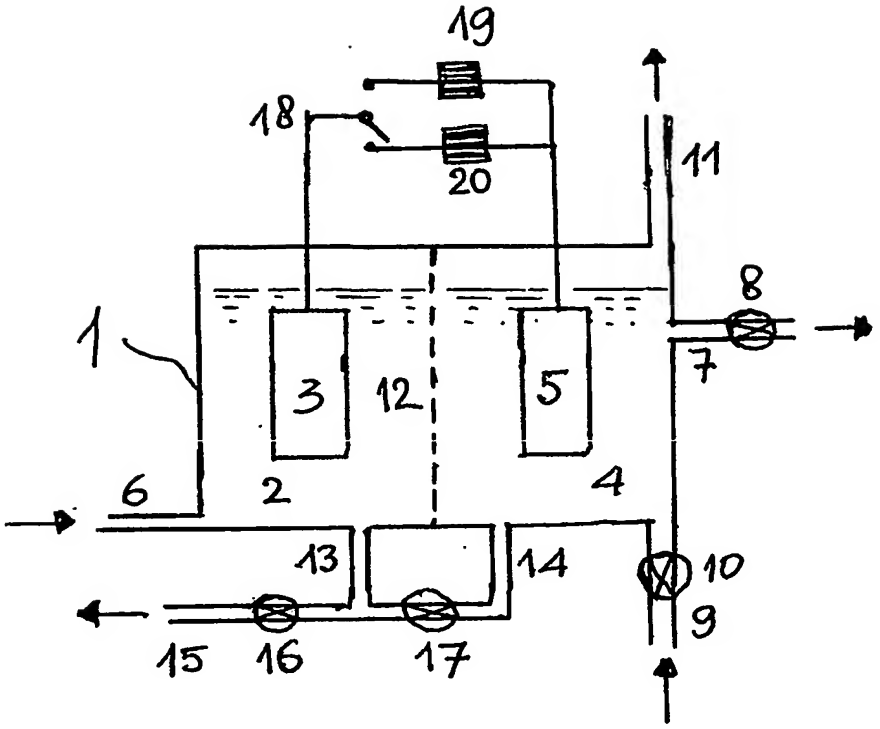

Fig.